# Composite Cathode Architectures Made by Freeze-Casting for All Solid-State Lithium Batteries

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# Overview

## Timeline

- Start: Apr. 2019
- End: Mar. 2021
- 50% complete

## Budget

- Total project funding: 667k
  - ❑ DOE: 600k
  - ❑ Industrial cost share: 67k

## Partners

- Montana State University (MSU)
- Mercedes Benz R&D North America (MBRDNA)

## Barriers*

- Performance/Life
  - ❑ Cell chemistries that provide higher energy have life and performance issues.
  - ❑ Higher energy cells are still one way to reduce costs.
  - ❑ Need improvement in extreme fast charge and low temperature performance.

*US DRIVE Electrochemical Energy Storage Technical Team Roadmap September 2017

# Relevance

## Impact

Solid-state-batteries using oxide solid electrolytes promise higher energy density with superior safety. We aim to construct solid-state-batteries with thick composite cathodes paired with lithium metal anodes. The architecture of the developed composite cathode may also provide superior rate performance and low temperature operation compared to lithium-ion batteries.

## Objectives

- Produce/characterize Al:$Li_7La_3Zr_2O_{12}$ (LLZO) porous scaffolds through freeze-tape-casting.
- Build thick composite cathodes by infiltrating an electronic conductor and high energy density cathode materials into the porous scaffolds.
- Construct solid-state-batteries by combining composite cathodes with a dense LLZO layer and a lithium anode.
- Fine-tune processing parameters to reach 500 Wh/kg.

# Milestones

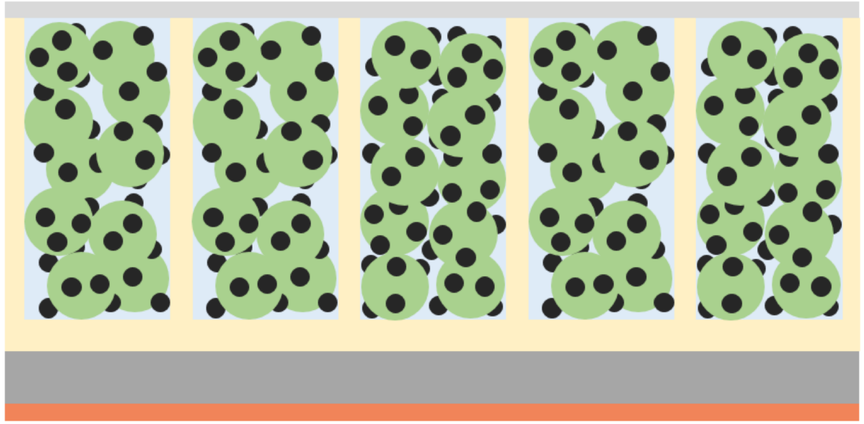
| Month/Year | Description | Owner | Status |
|---|---|---|---|
| Dec. 2019 | Build bilayer structures for cells, study sintering of bi-layers to achieve full cubic-LLZO phase. | LBNL/ MSU | Complete |
| Mar. 2020 | Assemble small cells and test | MBRDNA | Partially complete (Conducted at LBNL. CRADA paperwork with MBRDNA in progress) |
| Jun. 2020 | Vary porosity and morphology in scaffolds and study effects | LBNL/ MSU | On-schedule |
| Sep. 2020 | Optimize infiltration process | LBNL/ MSU | On-schedule |
| Dec. 2020 | Build trilayer structures for cells - stop if infiltration with anode material is too difficult or energy density is too low (go/no-go) | LBNL/ MSU | On-schedule |
| Mar. 2021 | Assemble small cells from optimized components and test | MBRDNA | On-schedule |

Any proposed future work is subject to change based on funding levels

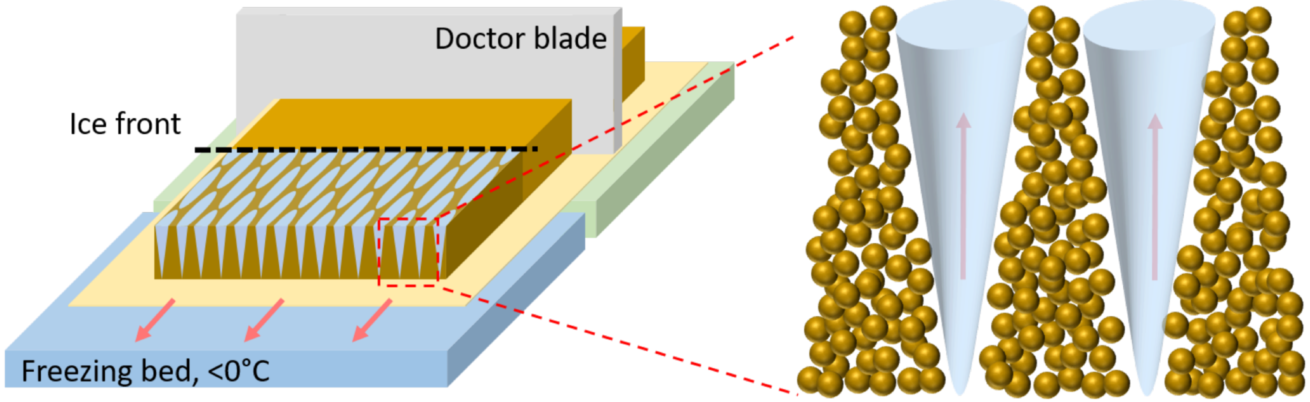
# Approach

- Construct thick composite cathodes by freeze-tape-casting and sintering of LLZO.
- The high porosity scaffolds with directional and continuous pore channels serve as an ideal host for cathode/anode components and aid infiltration during assembly.
- Construct porous/dense bi-layers and porous/dense/porous tri-layers of LLZO.
- Investigate scaffold porosity/pore morphology effect on battery performance.

**Goal**: Achieve high energy density oxide electrolyte based solid-state-batteries using lithium metal anode / high capacity cathode.



Proposed solid-state-battery architecture schematic



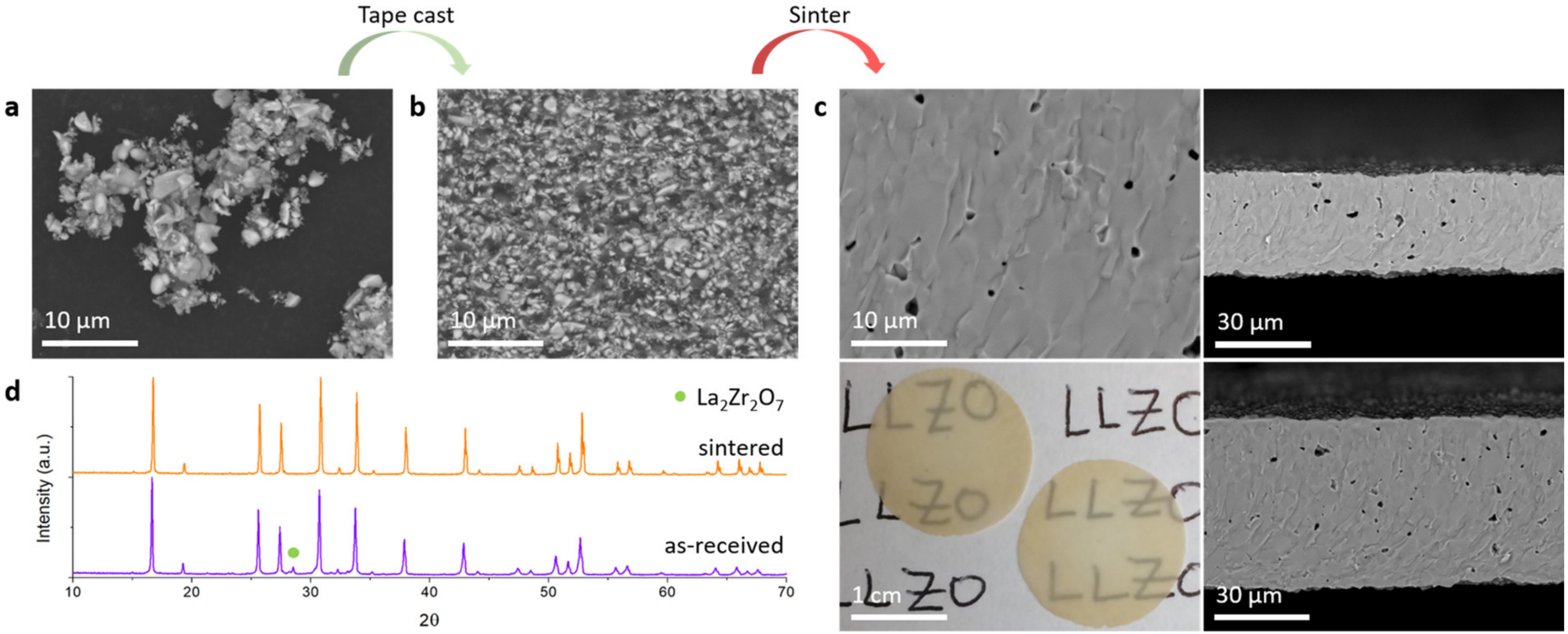

Schematic of freeze-tape-casting process

# Background

- During the Phase 1 of the Battery500 Seedling program (ended Jan. 2019), we investigated whether LLZO can be freeze-tape-cast and how processing parameters affect the obtained pore structures. Primary focus has been on processing of LLZO solid electrolyte and demonstrating a proof of concept cell.
- In Phase 2, we aim to build functioning solid-state-batteries using the freeze-tape-cast LLZO scaffolds as the cathode/anode host. Development in diverse aspects (cathode/LLZO interface, anode/LLZO interface, cathode powder selection, etc.) are required to achieve the goal of 500 Wh/kg.
- We use Ni-rich NMC cathode and lithium metal anode in accordance with the Battery500 program thrust.

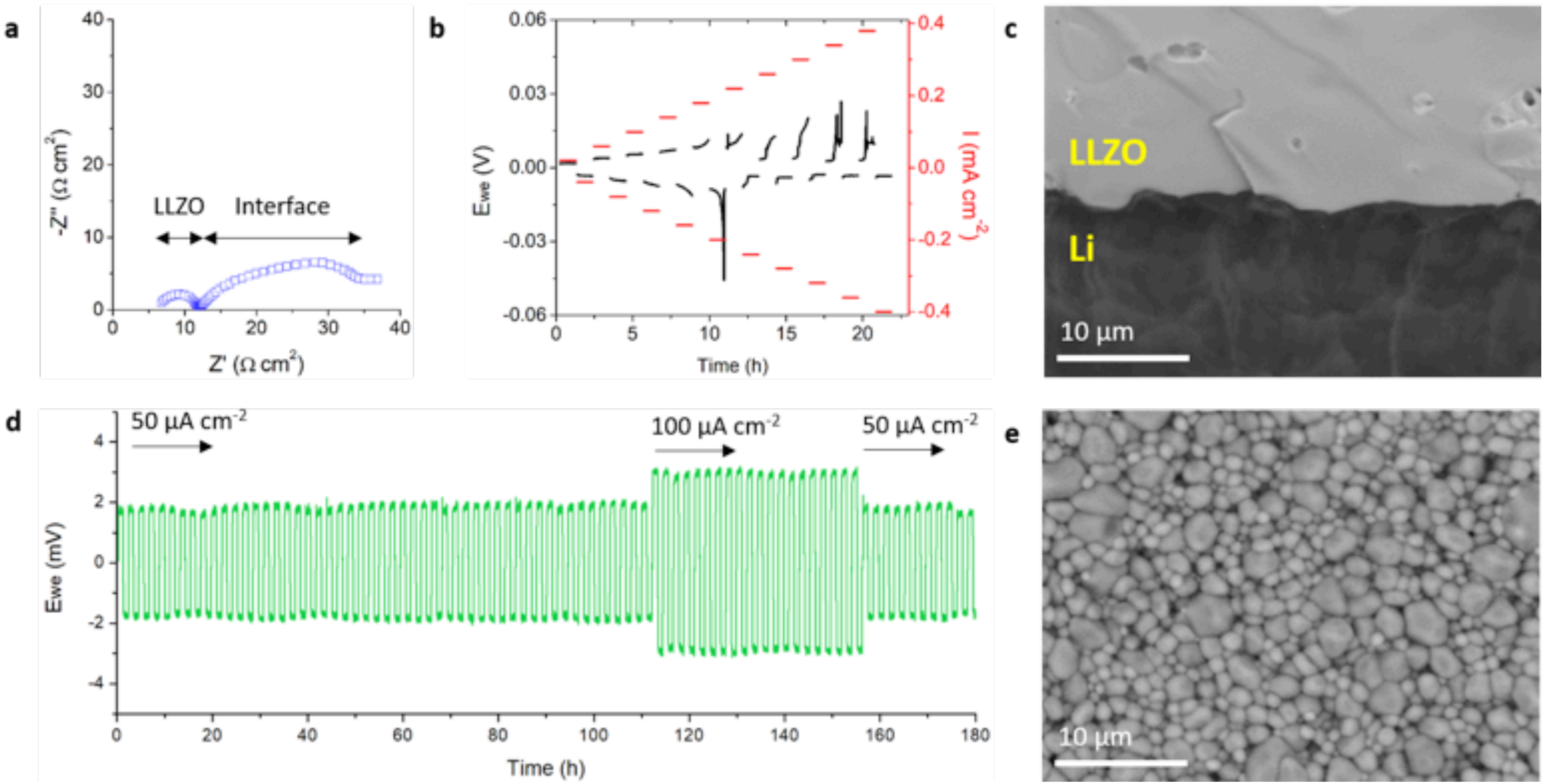
# Technical Accomplishments and Progress

Thin, dense, phase pure LLZO can be obtained through optimized ceramic processing.




The LLZO tape casting procedure was optimized by carefully controlling the time and temperature at which sintering was carried out. Freestanding tapes approximately 95% dense and 25-44 µm thick were made.

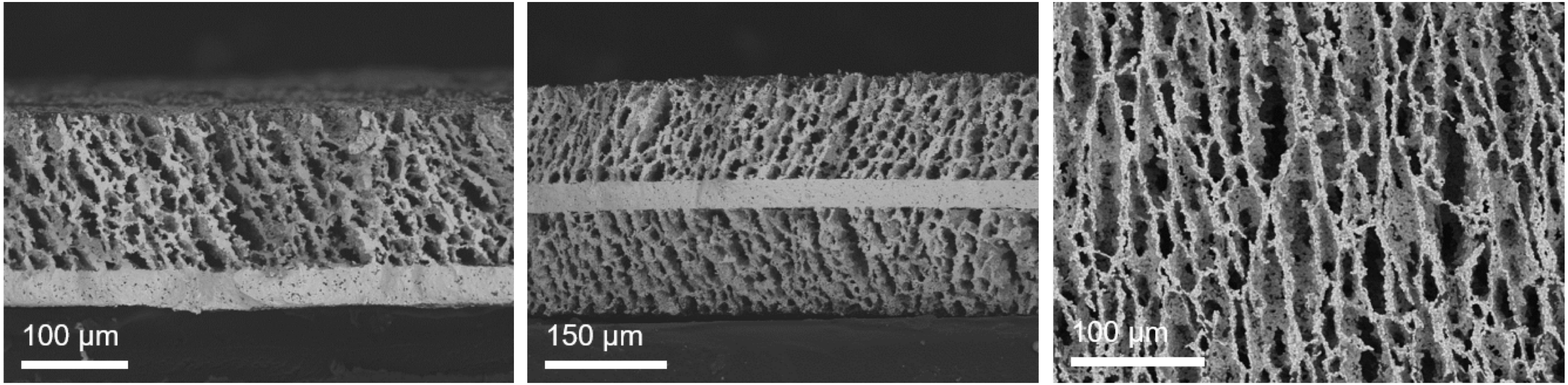
# Technical Accomplishments and Progress




Au was sputter coated on the LLZO dense layer to ensure good interfacial contact with lithium. This resulted in low interfacial impedance and acceptable critical current density in symmetrical cells.

# Technical Accomplishments and Progress

Porous/dense bilayers and porous/dense/porous trilayers of LLZO frameworks were produced by combining freeze-tape-casting and tape-casting.

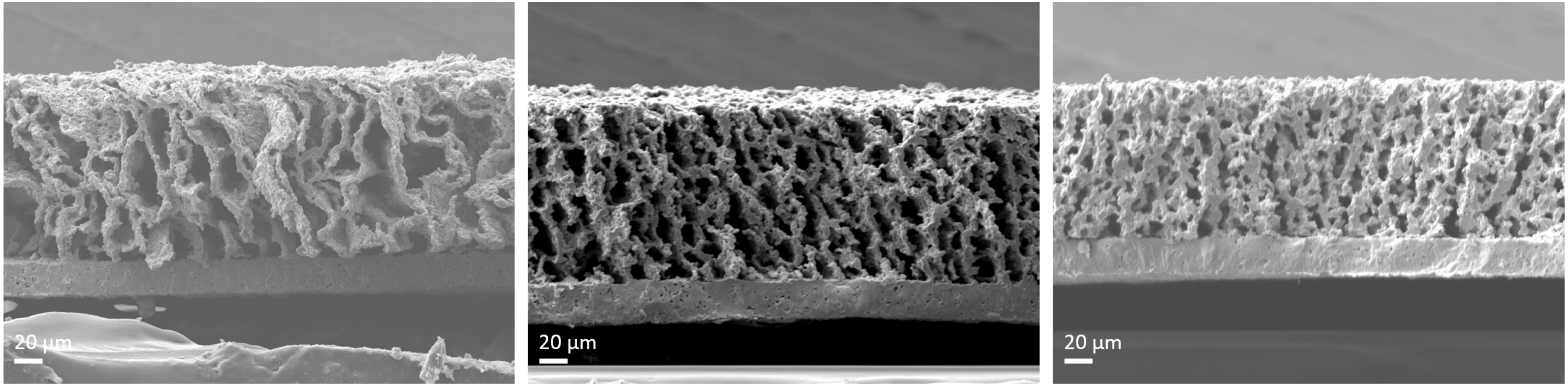



- Green tape-cast and freeze tape cast layers are sintered together to produce bilayers (left) or trilayers (middle) consisting of dense and porous layers.
- Heating schedule and excess lithium content are controlled to balance lithium loss on heating and achieve high conductivity cubic-LLZO phase.
- Surface pore openings and continuity of the pores through the thickness permit easy infiltration of cathode components.

# Technical Accomplishments and Progress

Scaffold porosities can be modified by adjusting the LLZO fraction of the freeze-tape-casting slurry.

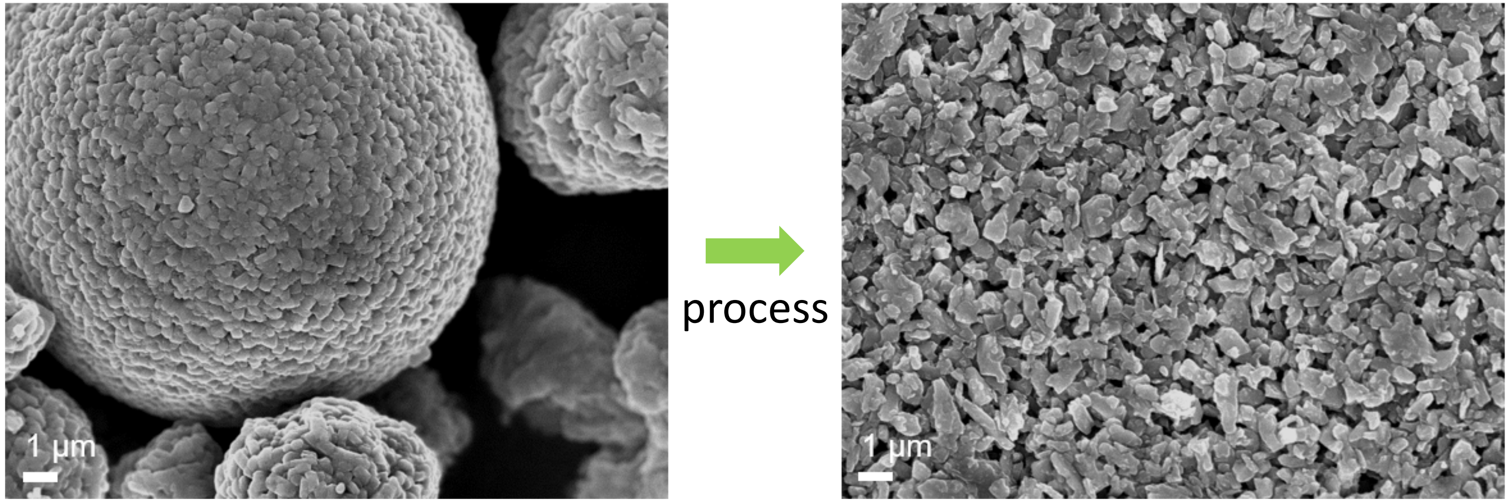
5% 7.5% 10%

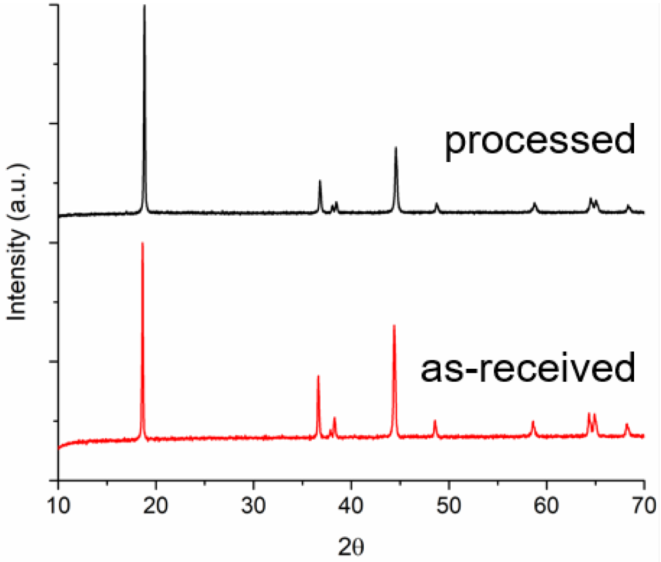


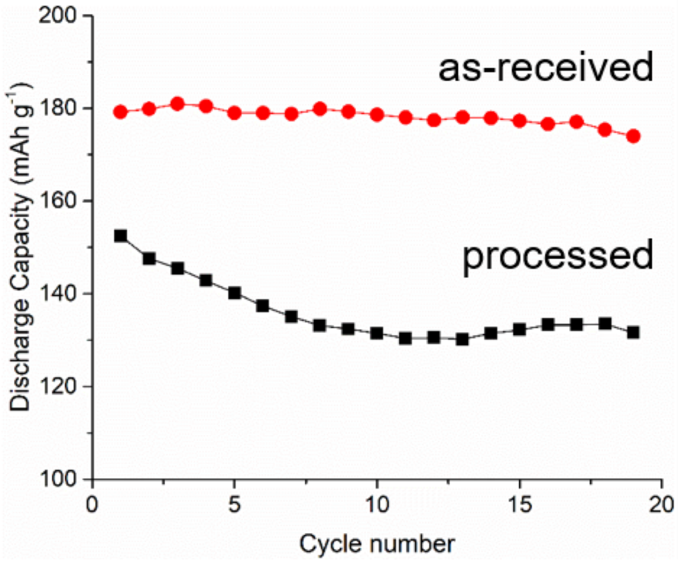

- LLZO volume fraction of the freeze-tape-casting slurry strongly affects the porosity of the sintered scaffolds.
- Excess lithium content and heating schedule had to be adjusted for each volume fraction samples in order to achieve the desired cubic-LLZO phase.

# Technical Accomplishments and Progress

Commercial cathode powders can be processed to smaller particle sizes for easier infiltration.



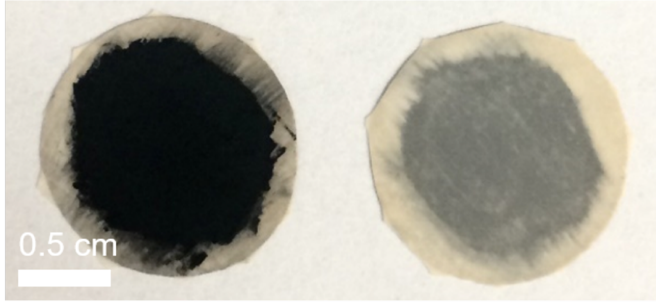



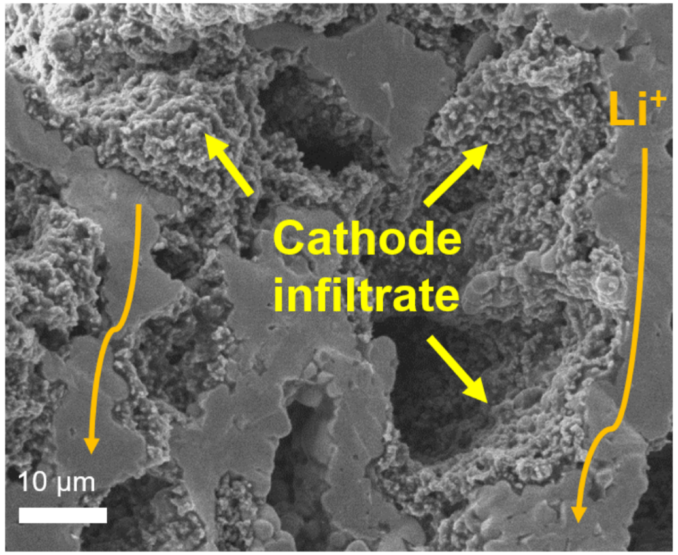

- Commercial NMC particles dispersed poorly and clogged the pores at the surface when slurry was infiltrated.
- As-received particles were ball-milled and heat-treated to break down the large secondary particles to small primary particles.
- The process successfully reduced the particle sizes but at the cost of capacity loss (lithium-ion-battery setup).

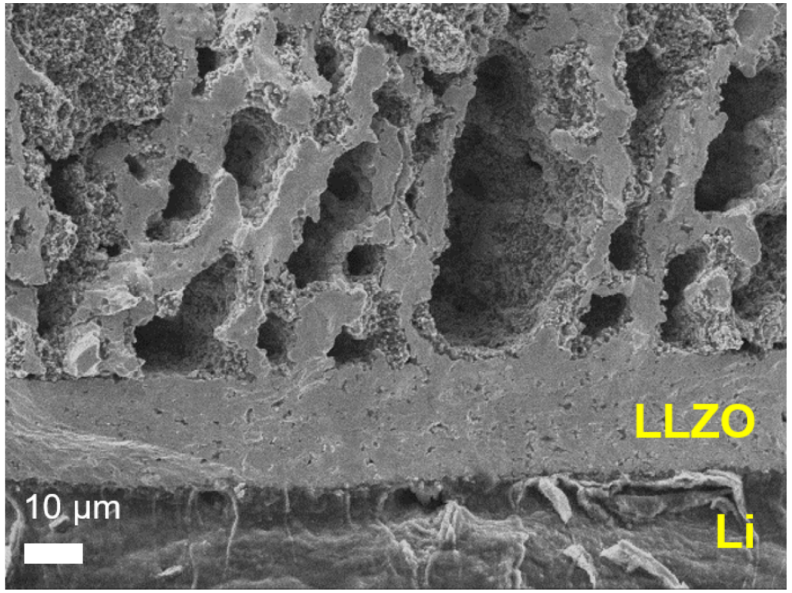
# Technical Accomplishments and Progress

Cathode components (cathode powder, binder, conductive additive) were introduced into the porous LLZO scaffold through slurry infiltration.




porous side dense side



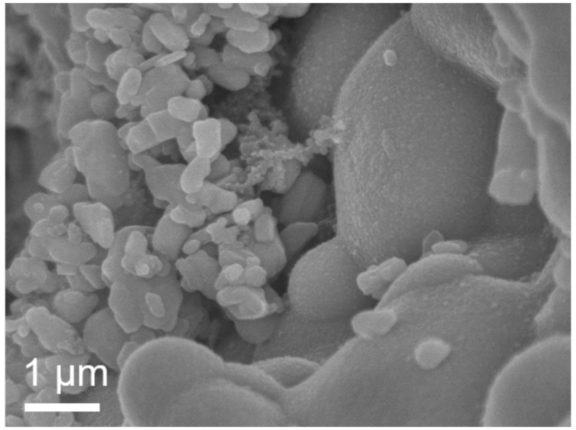




- Slurry containing processed NMC, carbon, and PVDF are infiltrated into the porous side of the porous/dense LLZO bilayer.
- Cathode components decorate the LLZO surface.

- Significant pore space still available. Requires further optimization and processing condition studies for higher filling rate.

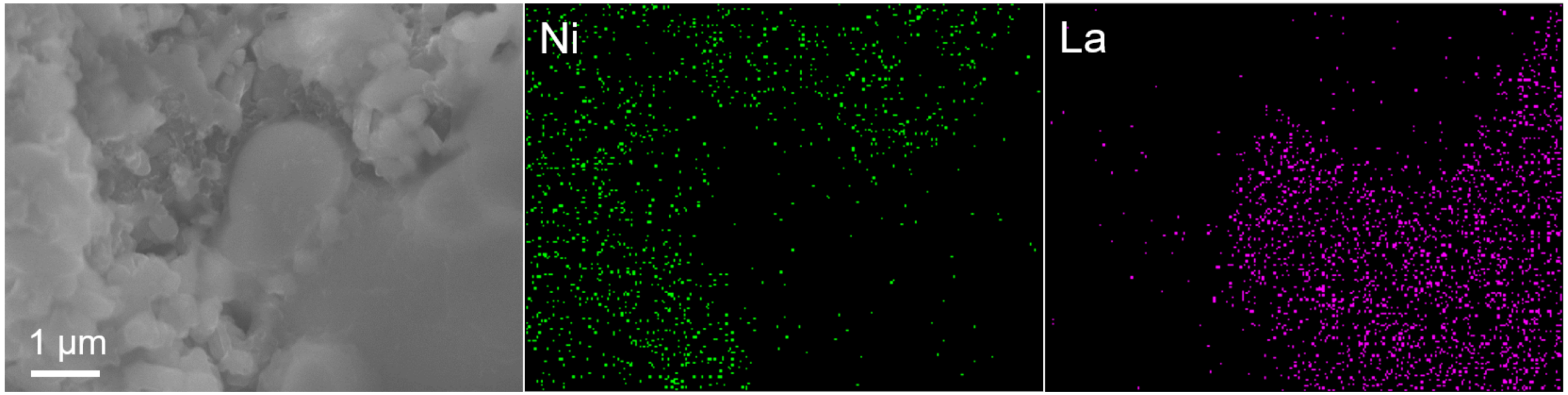
# Technical Accomplishments and Progress

Addition of secondary soft solid electrolyte aids electrochemical connection of cathode and LLZO solid electrolyte framework.




Cathode component infiltrated LLZO

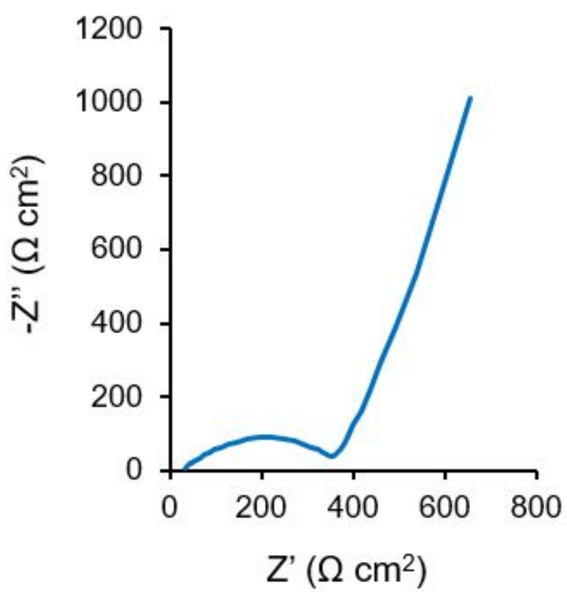
- Infiltrated cathode components (cathode powder, conductive additive, binder) do not form intimate contact with LLZO scaffold.
- Plastic-crystal based soft solid electrolyte was introduced to fill up the residual pore space and connect all components.

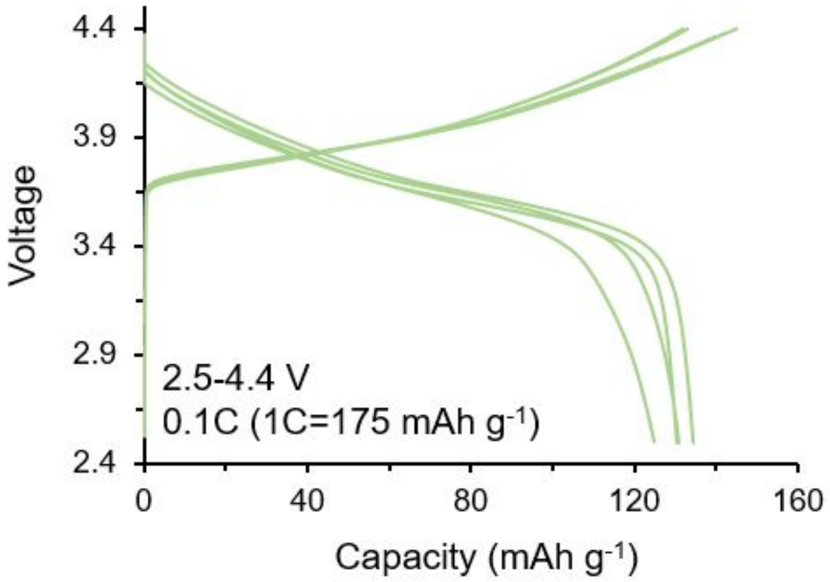



After soft solid electrolyte infiltration. Elemental distribution shows cathode (Ni) and LLZO (La) area.

# Technical Accomplishments and Progress

The constructed solid-state-batteries using NMC and Li metal pair operate at room temperature *without addition of liquid electrolyte*.

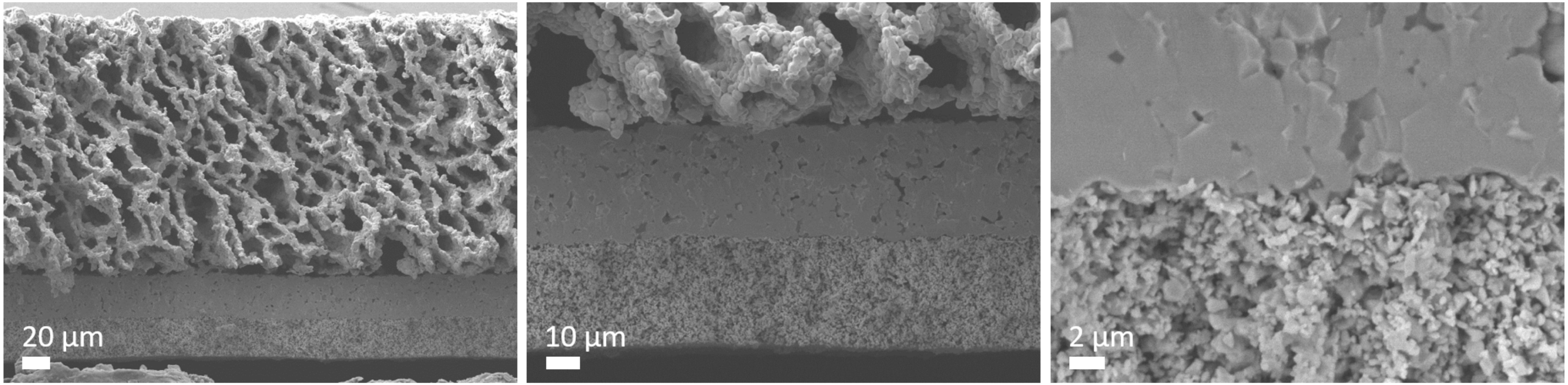



- Constructed solid-state-batteries had a low total cell impedance of 350 Ω $cm^2$. Those without plastic crystal solid electrolyte showed high impedance of 180 kΩ $cm^2$
- Cells were cycled between 2.5-4.4 V resulting in capacities of 125-135 mAh/g (cathode).
- First ever report of oxide electrolyte based true solid-state-battery with a practical form factor.

# Technical Accomplishments and Progress

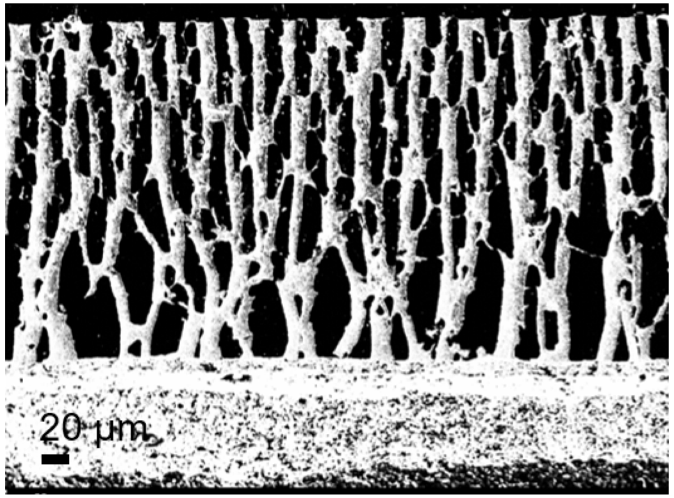
Trilayer LLZO framework incorporating one thin, porous LLZO layer is an alternative approach.



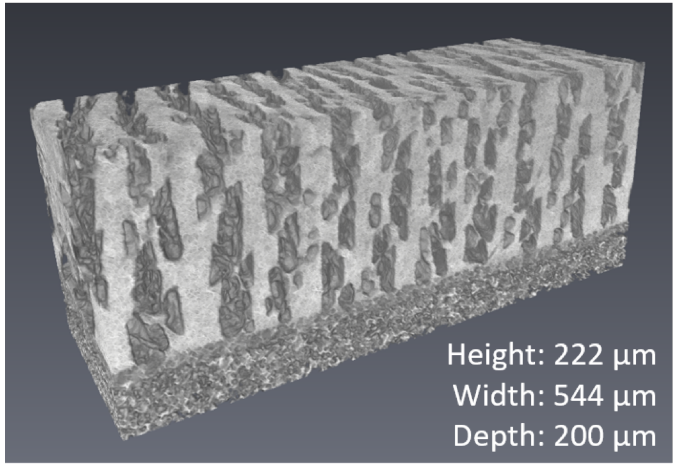

- A thin, porous LLZO layer made by drop-casting is attached to the dense side of the LLZO bilayer. This is an alternative approach to using a freeze-tape-cast layer on the anode side.
- Lower thicknesses can be achieved through the drop-casting method compared to freeze-tape-casting. This can help increase the energy density while also increasing the critical current density.

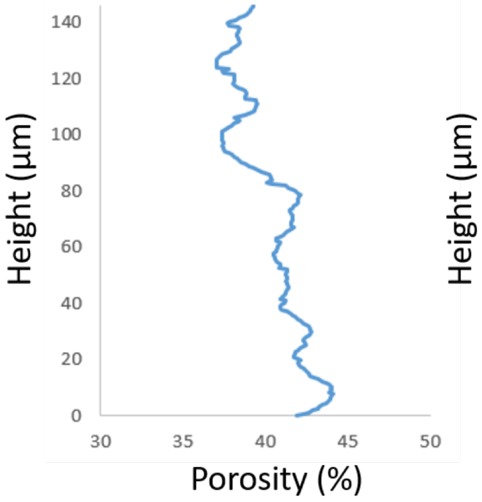
# Technical Accomplishments and Progress

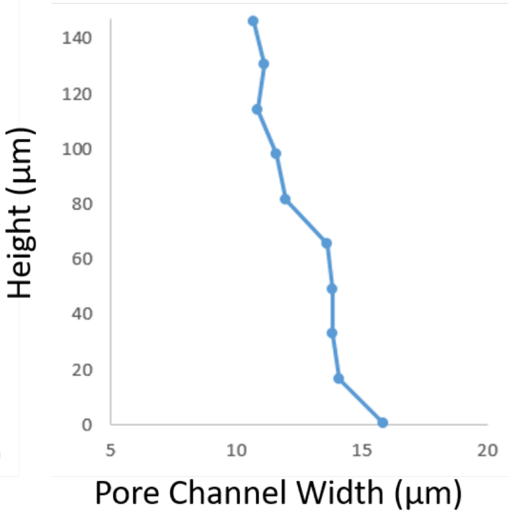
LLZO scaffolds with large, straight pore channels can be obtained through processing parameter changes.




- Large, straight pore channels can potentially make the infiltration process easier.
- Overall battery performance will differ based on the pore structure and porosity.



# Previous Year Reviewers' Comments

- Not available

# Collaboration and Coordination with Other Institutions

| Collaborator | Role |
|---|---|
| **Montana State University (Stephen Sofie)** | Freeze-tape-casting processing parameter screening/optimization. Collaborate on overall ceramic processing and cell build activities. |
| **Mercedes Benz R&D North America (Tobias Glossmann)** | Overall battery testing including industry protocols. |

# Remaining Challenges and Barriers

- **Low filling fraction of cathode components**
  The porous LLZO scaffolds remain mostly empty even after the infiltration of the cathode components.
- **Lower capacities of the processed cathode powders**
  Ball-milling and heat-treatment resulted in smaller particle sizes good for infiltration but caused capacity loss due to likely surface degradation.
- **What is optimum pore size?**
  Small pores are difficult to infiltrate, but large pores may mean poor contact among components
- **Lithium metal infiltration in trilayer configuration**
  Lithium metal was melt bonded to the dense LLZO layer of the bilayer using a sputter coated interfacial coating. Sputter coating does not provide 3D conformal coatings and hence the same method cannot be applied to porous LLZO.

# Proposed Future Work

- **Infiltration process optimization**
  Develop methods to fill most of the LLZO scaffold pore space.
- **High capacity cathode powders**
  Develop methods or find vendors/collaborators that can supply small particle size cathode powders. Or explore large pore size LLZO scaffold.
- **LLZO scaffold porosity/pore size modification**
  Widen the obtainable porosity/pore size range of the LLZO scaffolds. Work with modelers to determine best pore size
- **Conformal interfacial material coating on porous LLZO**
  Investigate methods to apply conformal interfacial coating materials to porous LLZO.
- **Solid-state cell build**
  Construct more solid-state-batteries using the above listed components and perform cycling tests.

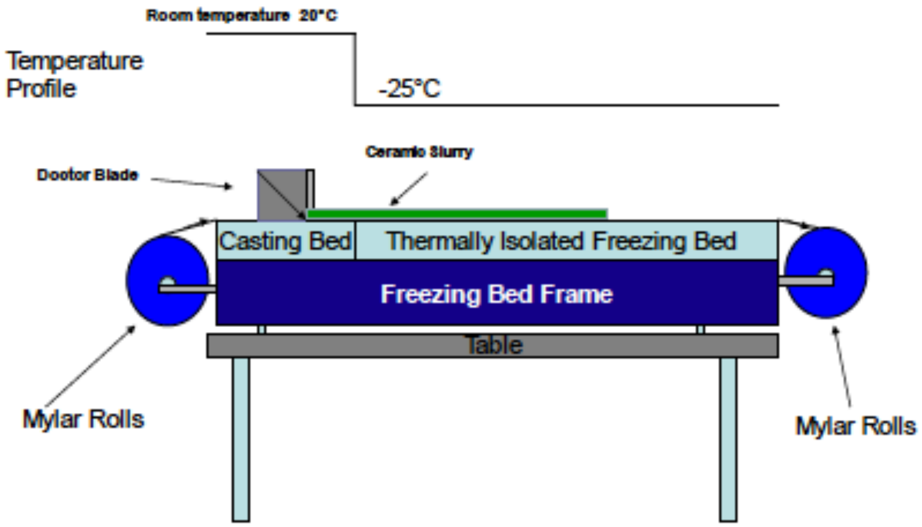
Any proposed future work is subject to change based on funding levels

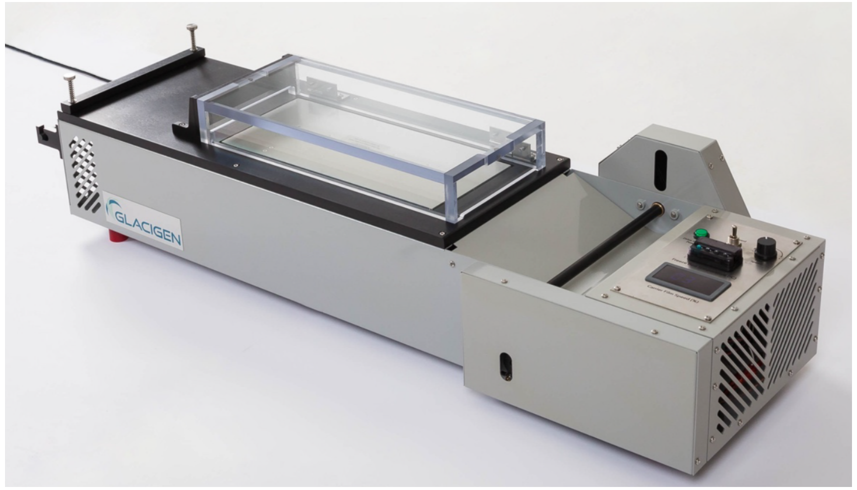
# Summary

- We continue to investigate various freeze-tape-casting conditions to modify pore structures and porosity.
- Porous/dense bilayers and porous/dense/porous trilayers of LLZO frameworks were successfully produced by combining freeze-tape-casting and tape-casting.
- Solid-state-batteries were constructed using a porous/dense bilayer LLZO framework. Cathode components were infiltrated into the porous side and lithium metal was bonded to the dense side to complete a cell.
- It was crucial to introduce a plastic crystal based soft solid electrolyte to connect cathode components to the LLZO framework and make the solid-state batteries operate.
- The constructed cells show low impedance (350 $\Omega$ $cm^2$) and decent initial capacities of 125-135 mAh/g.
- This is the first ever demonstration of a room temperature operational solid-state cell based on LLZO with a practical form factor. No added liquid electrolyte!

# Technical Back-Up Slides

# Freeze-tape-casting process




Batch prep. → Ball-mill → Ball-mill → Stir → Freeze tape cast → Freeze dry → Sinter

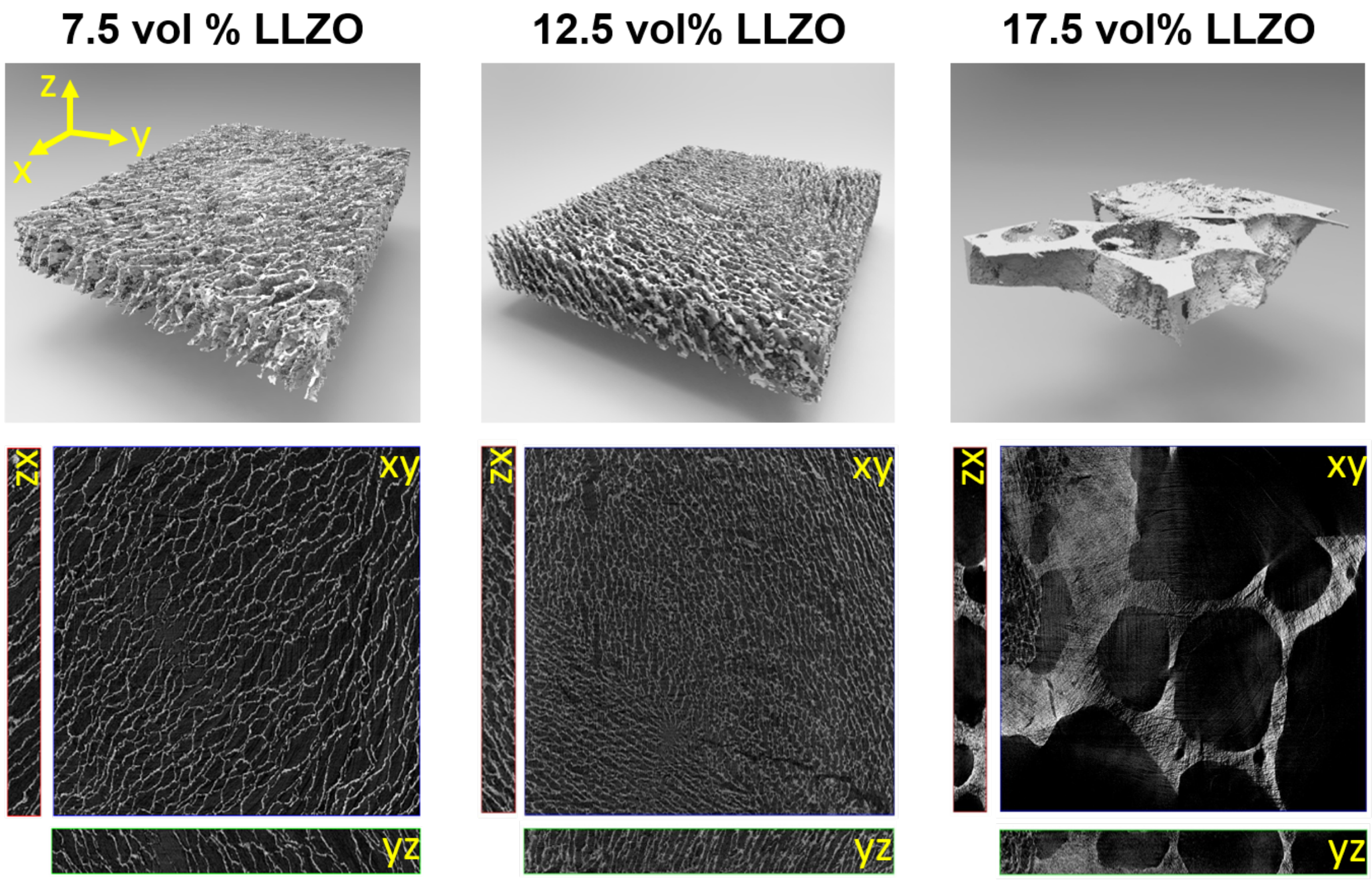
Batch prep.:
- LLZO
- $H_2O$
- Dispersant
- $ZrO_2$ beads

First ball-mill:
- Surfactant
- Defoamer
- Viscosity modifier

Second ball-mill:
- Emulsion binder

# Freeze-tape-cast LLZO scaffolds

LLZO volume fraction in the freeze-tape-casting slurry has a significant impact on the pore structure of the sintered scaffolds.



# Heating schedule sensitivity of LLZO

Excessive heating of LLZO can result in lithium-deficient secondary phases. Heating schedules have to be optimized to reach high density and phase purity concomitantly.